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16. ABSTRACT

In 1984, the Quality Assurance Division conducted the National Audits for Stationary Source Test Methods. The audit materials consisted of: a calibrated orifice for Method 5 (DGM only), five simulated liquid samples each for Method 6 (SO_2) and Method 7 (NO_x), two coal samples for Method 19A, and a disposable gas cylinder for Method 3 (Orsat analyzer). Participating laboratories sent their data to the Source Branch and in return received a written report comparing their results to EPA's.

In the Method 5 audit, the mean value for all participants differed by 3.1% from the expected (EPA) value. For the Method 6 audit, the average mean differed by 3.8% from the expected value, and in the Method 7 audit the average mean differed by 3.2%.

In the two coal audits, the parameters measured were sulfur, moisture, ash, and Btu content. On the average for the sulfur analysis, 82% of the participants measured within 10% of the expected value; for Btu, 97% of the participants measured within 10% of the expected value.

In the Method 3 audit, each parameter had only one concentration. The mean for CO_2 was 1.5% from the expected value. The mean for O_2 was 2.1%.

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A SUMMARY OF THE 1984 EPA NATIONAL PERFORMANCE AUDIT PROGRAM ON SOURCE MEASUREMENTS

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the environment, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection regulations through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Environmental Protection Agency, including the Office of Air and Radiation, and the Office of Toxic Substances.

The major task of this study was to report the results of the national quality assurance audit program for stationary source test methods. Audits were designed to estimate the minimal analytical and computational accuracy that can be expected with EPA Method 5 (dry gas meter only), Method 6 (sulfur dioxide), Method 7 (nitrogen oxides), Method 19 (coal), and Method 3 (carbon dioxide and oxygen). Statistical analysis was used to characterize the data.

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ABSTRACT

In 1984, the Quality Assurance Division conducted the National Audits for Stationary Source Test Methods. The audit materials consisted of: a calibrated orifice for Method 5 (dry gas meter only), five simulated liquid samples each for Method 6 (SO_2) and Method 7 (NO_x), two coal samples for Method 19A, and a disposable gas cylinder for Method 3 (Orsat analyzer). Participating laboratories sent their data to the Source Branch and in return received a written report comparing their results to EPA's.

In the Method 5 audit, the mean value for all participants differed by 3.1% from the expected (EPA) value. For the Method 6 audit, the average mean differed by 3.8% from the expected value. The average mean in the Method 7 audit was 3.2% from the expected value.

In the two coal audits, the parameters measured were sulfur, moisture, ash, and Btu content. On the average for the sulfur analysis, 82% of the participants measured within 10% of the expected value; for Btu, 97% of the participants measured within 10% of the expected value.

In the Method 3 audit, each parameter had only one concentration. The mean for CO_2 was 1.5% from the expected value. In this audit, the mean for O_2 was 2.1% from the expected value.

This report includes the results of the performance audits done during the period from January through December 1984.

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We express our appreciation to the laboratories that participated in the National Performance Audit Program for Stationary Sources. Thanks also to the Standards Laboratory/Performance Evaluation Branch/Environmental Monitoring Systems Laboratory (EMSL), who did the acceptance testing of the audit samples, and to the programmers of the Monitoring and Assessment Division/EMSL for providing the data systems to store and evaluate the data.

Section 1

INTRODUCTION

The Environmental Protection Agency's Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, NC, established an audit program in 1977 to evaluate the performance of companies that conduct compliance testing using EPA reference methods. The audits check the participants' analytical accuracy in applying the analytical phase of EPA Reference Methods 3, 6, 7, and 19A and the calibration accuracy of the Method 5 control console (1). Accuracy is defined as the percent difference between the participant's analytical results and the EPA expected value. By participating in this free and voluntary program, testing companies can compare their performance to other laboratories conducting similar measurements.

Source Test Methods 3, 5, 6, and 7 were each audited once and Method 19A twice in 1984. Each participating laboratory received an audit package consisting of the audit sample, a data card, instructions, and an envelope for returning the data to EPA. A label for returning the audit device was included with the Method 5 audit package. Participants had eight weeks to use the audit material and return their data to EPA. At the end of this period all data received were statistically analyzed to determine the precision (repeatability or reproducibility) and accuracy with respect to the EPA expected value obtained by the participants. (See Appendix A.)

The Quality Assurance Division of EMSL maintains a repository of audit samples for the EPA Methods 3, 6, 7, and 19A. These samples are available to source testing laboratories for such purposes as training new personnel or conducting quality control checks. Since the expected values for these samples are included with the analysis instructions, there is no requirement for the data to be returned to EPA. We recommend that source testing laboratories use this sample repository to help improve their overall analytical performance.

This report summarizes the results obtained in the 1984 source audits.

Section 2

SUMMARY

In 1984, EPA's EMSL, Research Triangle Park, North Carolina, conducted National Quality Assurance Audits for Stationary Source Test Methods 5 (dry gas meter only), 6 (SO_2), 7 (NO_x), 19A (coal), and 3 (Orsat analyzer). Industrial laboratories, contractors, foreign laboratories, as well as local, State, and federal agencies participated.

The results of the 1984 Method 3 audit are summarized in Table 1. Participants analyzed the gas sample twice for percentage of carbon dioxide, oxygen, and carbon monoxide. The mean values of carbon dioxide and oxygen differed by 2% from the expected value. In contrast, the mean values for carbon monoxide differed as much as 21% from the expected value.

TABLE 1. PARTICIPANTS' RESULTS FROM METHOD 3 AUDIT
(ALL DATA - NO OUTLIERS REMOVED)

Type of Sample	Audit Date	Parameter	No. of Analyses	Replicate	EPA (True) Value	Participant Results		
						Mean	Median	Std. Dev.
Small Cylinder (Gas)	0784	% CO_2	64	1	8.00	7.88	7.80	0.65
			62	2	8.00	7.91	7.80	0.59
		% O_2	64	1	9.90	10.11	10.00	1.22
			62	2	9.90	10.06	10.00	1.21
		% CO	51	1	0.70	0.55	0.60	0.19
			50	2	0.70	0.57	0.60	0.19

One Method 5 audit was conducted in 1984. The overall results (no outliers removed) are summarized in Table 2. The mean for all participants was 3.1% from the expected value. After correcting for outliers, the mean was 2.2%. The participants' performances did improve from previous audits in that the standard deviation greatly decreased (2, 3, 4).

TABLE 2. PARTICIPANTS' RESULTS FROM METHOD 5 AUDITS
(ALL DATA - NO OUTLIERS REMOVED)

Type of Sample	Parameter	Audit Date	No. of Analyses	Mean (% from EPA Value)	Median	Std. Dev.
Orifice	Volume	0684	631	3.1	1.9	4.9

Table 3 presents the data (no outliers removed) from the Methods 6 and 7 audits. In the Method 6 audit, the procedure requires the participants to determine the sulfate content in five aqueous solutions using the titration procedure. For each concentration, the mean of the participants was 5% higher than the expected value. In contrast, the median differed by 1%. In the Method 6 audit, 50 to 70% of the participants achieved an accuracy within 2% of the expected value. Also, the standard deviation is proportional (~30%) to the mean level of the sulfate samples.

TABLE 3. PARTICIPANTS' RESULTS FROM METHODS 6 AND 7 AUDITS
(ALL DATA - NO OUTLIERS REMOVED)

Type of Sample	Audit Date	No. of Analyses	EPA True Value (mg/DSCM)	Participant Results		
				Mean	Median	Std. Dev.
Aqueous Sulfate	0584	92	282.2	296.3	284.0	83.74
		91	297.4	312.7	299.8	94.59
		92	899.9	924.3	890.3	277.30
		92	968.5	999.2	966.8	301.92
		92	1197.3	1234.8	1192.5	377.38
Aqueous Nitrate	0484	71	91.0	96.3	90.4	36.07
		70	102.4	111.1	100.5	49.50
		70	284.4	288.0	280.0	64.95
		71	466.4	464.9	457.9	117.78
		70	523.3	523.2	517.5	104.37

The Method 7 audit procedure requires that the participants determine the nitrate content in five aqueous solutions. For each concentration, the mean of the participants was not higher than 8% from the expected value; but in contrast, the median differed by less than 2%. In this audit, 31% to 46% of the participants achieved an accuracy within 3% of the expected value for 4 out of 5 samples. However, on the lowest concentration sample only 21% achieved this accuracy.

Table 4 summarizes the results of the two coal audits that were conducted in 1984. Participants analyzed each coal sample in duplicate for percentage of sulfur, moisture, and ash, and for gross calorific value (Btu/lb). The means of the ash, moisture, and sulfur content were within 5% of the expected value on both concentrations. An accuracy of 1% was achieved on the Btu content.

TABLE 4. PARTICIPANTS' RESULTS FROM METHOD 19A COAL AUDITS
(ALL DATA - NO OUTLIERS REMOVED)

Type of Sample	Audit Date	Parameter	No. of Analyses	EPA Value	Participant Results		
					Mean	Median	Std. Dev.
Coal	0384	% S	113	0.45	0.45	0.46	0.23
	0984		100	1.17	1.18	1.17	0.11
	0384		113	3.28	3.04	3.06	0.29
	0984		99	2.93	2.84	2.83	0.22
	0384	% H_2O	114	2.94	2.92	2.95	0.44
	0984		102	1.86	1.90	1.97	0.33
	0384		114	12.01	11.85	12.16	1.52
	0984		101	10.65	10.44	10.79	1.50
	0384	% Ash	112	9.45	9.46	9.50	0.47
	0984		101	9.74	9.90	9.67	2.32
	0384		112	13.13	13.04	13.13	1.00
	0984		100	12.87	12.75	12.80	1.07
	0384	Btu/lb	110	12115.0	12020.3	12133.0	385.99
	0984		95	12595.0	12504.3	12631.0	409.65
	0384		110	13135.0	13068.9	13087.0	105.50
	0984		96	13710.0	13850.7	13860.0	224.92

Section 3

METHOD 3 AUDIT

This audit checks the participants' ability to analyze a gas sample using an Orsat analyzer. The audit package consists of a disposable cylinder that contains a 4-liter sample of oxygen, carbon dioxide, and carbon monoxide. The analyst expels the gas into the Orsat analyzer using the positive pressure of the cylinder. The gas sample is quantitatively analyzed for percentage of carbon dioxide, oxygen, and carbon monoxide.

In the 1984 audit, 50% of the 109 laboratories receiving the audit package returned data. Table 5 shows the total number of laboratories requesting participation versus the number that returned data for the Method 3 audit.

TABLE 5. METHOD 3 AUDIT PARTICIPANTS

Category	No. Receiving Samples 0784	No. Returning Data 0784
Contractor	57	21
Industry	32	20
Foreign	1	1
Federal	2	1
State	14	8
Local	3	3
Total	109	54

Table 6 summarizes the Method 3 audit results. Each laboratory was asked to analyze the sample in duplicate. Five and ten percent accuracy were chosen for the precision reporting criteria for each of the parameters. Each parameter had only one concentration.

In the 1984 audit, 82% of the reporting laboratories achieved an accuracy within 5% for the CO_2, which was a 34% increase from the last audit (4). Eighty percent of the laboratories achieved an accuracy within 5% of the expected value for the O_2 analysis. For the CO analysis, only 18% of the laboratories achieved an accuracy within 5%, and 19% of the laboratories did not report a value for CO.

TABLE 6. SOURCE METHOD 3 AUDIT - 0784

Expected Value	No. of Analyses	Laboratories Accurate within ± 5%	Laboratories Accurate within ± 10%
		CO_2	
8.00	(1) 64	80%	92%
	(2) 62	85%	94%
		O_2	
9.90	(1) 64	78%	94%
	(2) 62	81%	95%
		CO	
0.70	(1) 51	18%	18%
	(2) 50	10%	10%

Section 4

METHOD 5 DRY GAS METER AUDIT

In the Method 5 audit procedure, the participants use a calibrated orifice to check the calibration of the dry gas meter in their EPA Method 5 control console (meter box). They insert the orifice in the Method 5 meter box, allow the box to warm up, and then make three 15-minute volume measurements. The participants convert each of the three volumes to cubic meters at standard conditions using the formula specified in Eq. 5.1 of Method 5 (Appendix A 40 CFR 60) and record them on the data card. Finally, they return the orifice and the data card to EPA, where the data undergoes statistical analysis.

In the 1984 audit, 62% of the 155 laboratories that received the audit package returned data. This percentage was slightly lower than those responding in previous audits (2, 3, 4). Table 7 shows the categories of the participants and compares the number of participants who requested participation in the Method 5 audit with the number who actually returned data.

TABLE 7. METHOD 5 AUDIT PARTICIPANTS

Category	No. Receiving Samples 0684	No. Returning Data 0684
Contractor	78	45
Industry	51	31
Foreign	4	3
Federal	2	2
State	15	12
Local	5	3
Total	155	96

Figure 1, a cumulative histogram, shows the accuracy obtained by participants in the Method 5 audit, expressed as the percent difference from the expected (EPA) value at various levels of accuracy. The Code of Federal Regulations (1) requires that the dry gas meter be calibrated within an accuracy of ±2%. Figure 2 shows that 54% of the reporting laboratories attained this accuracy. These results are an improvement compared to three years ago, but may now be leveling off. Table 8 is a summary of previous audits which, like Figure 2, shows improvement over the past three years.

TABLE 8. PREVIOUS RESULTS OF METHOD 5 AUDIT

Audit	Number of Analyses	Mean (% from EPA Value)	Median (% from EPA Value)	Std Dev
0381	738	13.6	2.7	110.2
0981	723	4.3	2.5	9.7
0382	827	7.6	2.5	39.5
0982	769	12.5	2.5	81.4
0383	763	5.7	2.2	32.7
0983	614	4.1	1.9	21.3
0684	631	3.1	1.9	4.9

The histogram in Figure 3 compares the individual results from all participants of the 1984 audit with the mean and median values. The majority of the laboratories reported values lower than the EPA value. The standard deviation of the triplicate analysis (repeatability) by each laboratory indicated that 75% of the standard deviations for each set were within 0.3%. Four percent of the 1984 data were identified as outliers using Chauvenet's Criterion (5). Before the outliers were removed, the mean value differed by 3.1% from the expected value. After deletion of outliers, this value was reduced to 2.2%.

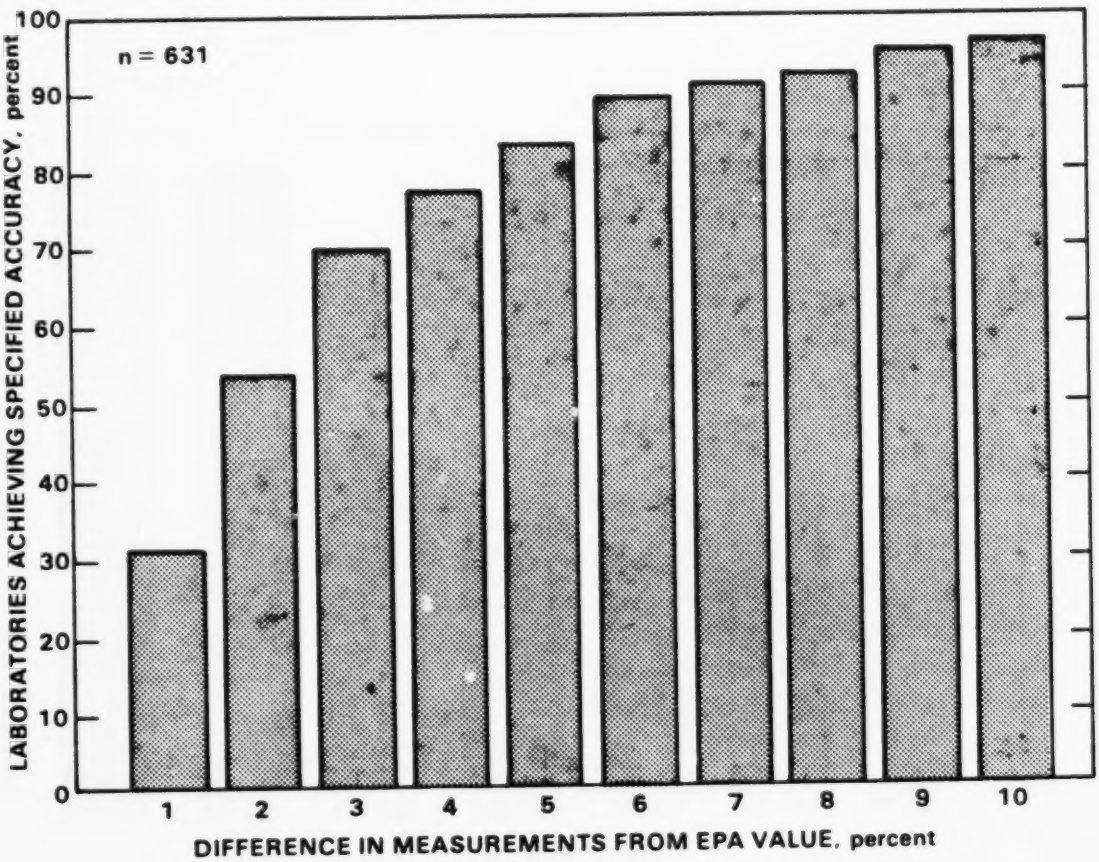

Figure 1. Cumulative accuracy for participants in method 5 audit, 0684.

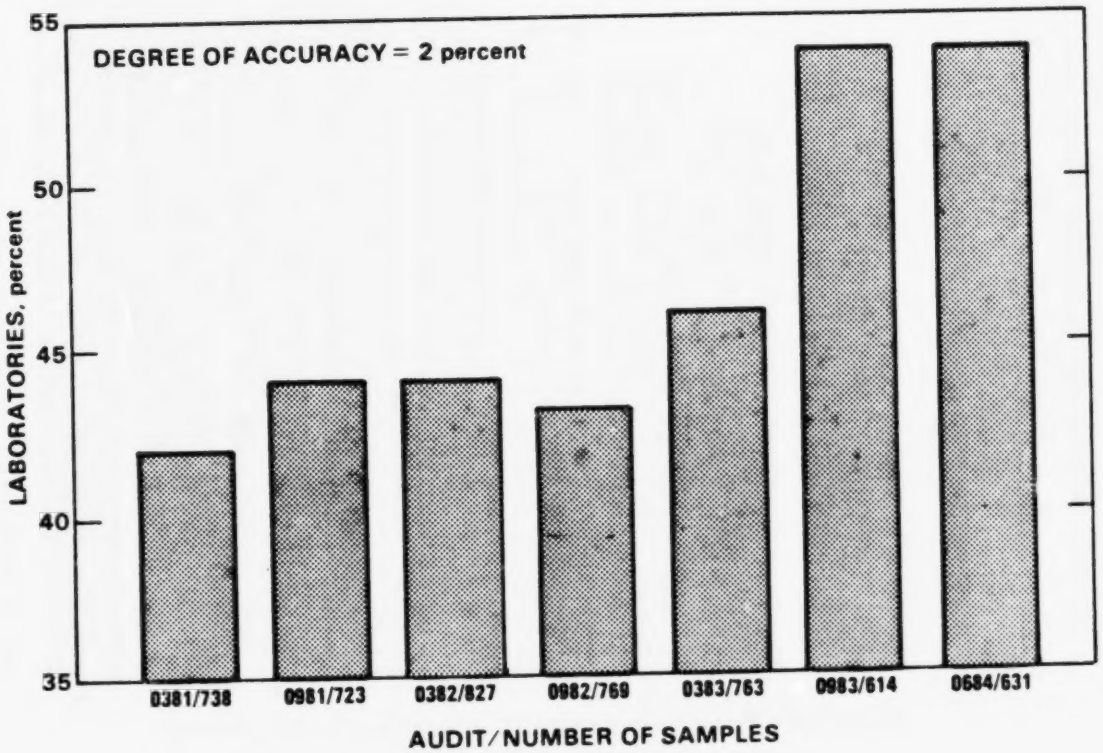

Figure 2. Laboratories within 2 percent accuracy.

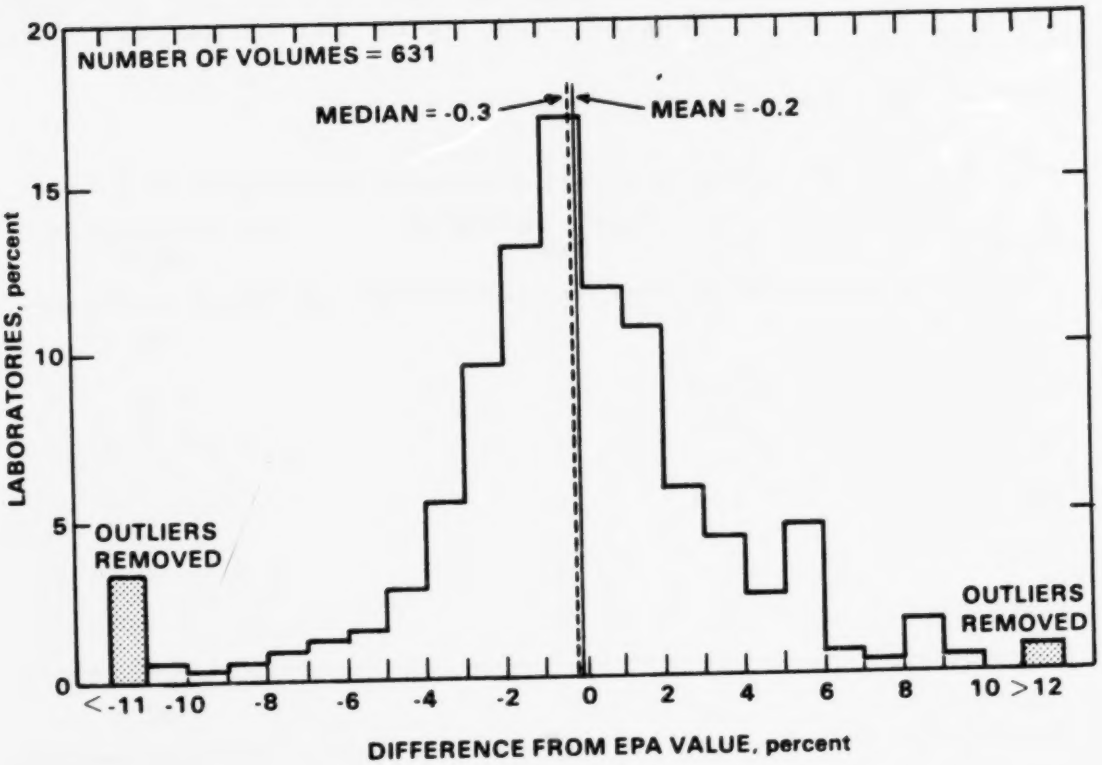

Figure 3. Results of Method 5 audit 0684.

Section 5

METHOD 6 AUDIT

This audit checks the participants' ability to quantitatively analyze Method 6 samples for sulfate content. The audit set consists of five aqueous dilutions of 10 N sulfuric acid in 25 ml sealed glass ampoules. The analyst withdraws 5 ml from each ampoule, adds 30 ml of 3% hydrogen peroxide, and dilutes this sample to 100 ml with distilled water. A 20-ml aliquot is then withdrawn from the diluted sample, 80 ml of 100% isopropanol and thorin indicator are added, and the sample is titrated with barium perchlorate ($Ba[ClO_4]_2$) to a pink endpoint. In calculating the results, the participants assume an original sample volume of 100 ml, and a sample volume of 0.021 dry standard cubic meter of stack gas.

Table 9 shows the categories of the participants and compares the total number of participants requesting participation with the number returning data. In the 1984 audit, 59% of the 157 laboratories that received the audit package returned data.

TABLE 9. METHOD 6 AUDIT PARTICIPANTS

Category	No. Receiving Samples 0684	No. Returning Data 0684
Contractor	79	40
Industry	49	31
Foreign	5	3
Federal	1	1
State	15	11
Local	8	6
Total	157	92

Table 10 shows the percentage of laboratories that achieved 2% and 5% accuracy for each of the five different concentrations in the Method 6 audit. Also, at least 50% of the reporting laboratories achieved an accuracy within 2% for the three lower concentrations, but showed an improvement of 65% for the higher concentrations. Seventy-five percent of the laboratories were able to achieve an accuracy level of within 5% on all five samples.

TABLE 10. SUMMARY OF SOURCE SO_2 AUDIT

Concentration	0584	
	± 2%	± 5%
282.2 mg/DSCM	50%	79%
297.4 mg/DSCM	48%	76%
899.9 mg/DSCM	55%	88%
968.5 mg/DSCM	63%	88%
1197.3 mg/DSCM	70%	91%
n	92	

Section 6

METHOD 7 AUDIT

This audit checks the participants' ability to quantitatively analyze Method 7 samples for nitrate content. The NO_x audit set consists of five aqueous dilutions of a potassium nitrate (KNO_3) solution in 25 ml glass ampoules which are autoclaved after sealing so that bacteria which might attack the nitrate are destroyed. The analyst withdraws 5.0 ml of solution from an ampoule, adds this with 25 ml of the Method 7 absorbing solution to a flask, adjusts the pH with sodium hydroxide, and dilutes to 50 ml with distilled water. A 25-ml aliquot is withdrawn from the diluted sample, placed in an evaporating dish, and analyzed as described in Section 4.3 of Method 7 (1). After this treatment is completed, the absorbance is measured at 410 nm with a calibrated spectrophotometer. In calculating the concentrations present, the participant assumes that 2000 ml of stack gas was sampled.

Table 11 shows the total number of laboratories requesting participating in and the number that returned data for the 1984 Method 7 audit. Sixty percent of the 118 laboratories receiving the audit package returned data.

TABLE 11. METHOD 7 AUDIT PARTICIPANTS

Category	No. Receiving Samples 0484	No. Returning Data 0484
Contractor	66	36
Industry	37	23
Foreign	3	2
Federal	1	1
State	7	5
Local	4	4
Total	118	71

The percentage of laboratories that achieved 5 and 10% accuracy for each of the five concentrations are shown in Table 12. In addition, 40% of the reporting laboratories achieved an accuracy within 5% on the lowest concentrations and 55% achieved within 5% on the highest three concentrations. Seventy percent of the 71 laboratories were able to achieve an accuracy within 10% on all five samples.

TABLE 12. SUMMARY OF SOURCE NO_x AUDIT

Concentration	0484	
	± 5%	± 10%
91.0 mg/DSCM	38%	68%
102.4 mg/DSCM	49%	66%
284.4 mg/DSCM	53%	74%
466.4 mg/DSCM	54%	77%
523.3 mg/DSCM	63%	79%
n	71	

Section 7

METHOD 19A COAL AUDIT

Standards of performance for newer electric utility steam generators (Subpart Da of 40 CFR 60) allow coal sampling and analysis to serve as an acceptable method for determining scrubber inlet flue gas sulfur concentration. The coal audit checks the participants' ability to analyze coal samples for sulfur, ash, moisture, and Btu content.

Coal audit samples consisted of two bottles, each containing 50 grams of 60-mesh coal. The following American Society for Testing and Materials (ASTM) procedures (6) were recommended, but not required, for participants' use in analyzing the coal samples:

- ASTM D-3177 (Standard Test Method for Total Sulfur in the Analysis of Coal and Coke);
- ASTM D-3174 (Standard Test Method for Ash in the Analysis Sample of Coal and Coke);
- ASTM D-3173 (Test for Moisture in the Analysis Sample of Coal); and
- ASTM D-2015 (Standard Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Method).

The participants measured the parameters and reported their results for moisture (%) on an as-received basis, and their results for sulfur (%), ash (%), and gross calorific value (Btu/16) on a dry basis.

In both audits, 83% of the laboratories that received the audit package returned data. Seventy-two of the same laboratories participated in both audits and returned data. Table 13 shows the total number of laboratories requesting participation versus the number that returned data for coal audits 0384 and 0984.

TABLE 13. COAL AUDIT PARTICIPANTS

Category	No. Receiving Samples 0384	0984	No. Returning Data 0384	0984
Contractors	59	41	42	35
Industry	40	47	38	38
Federal	0	1	0	0
State	12	13	11	11
Local	5	4	5	4
Total	116	106	96	88

Tables 14 and 15 summarize the coal audit results. The number of analyses is greater than the number of participants because some companies had more than one laboratory participating. In this case, each laboratory received its own set of samples and was asked to analyze the samples in duplicate. Accuracies of 5% and 10% were chosen as the reporting criteria for each of the four parameters (sulfur, moisture, ash, and gross calorific content).

In the 0384 audit, 60% of the laboratories were able to analyze the sulfur content of the low level sample within 10% of the expected value; however, 86% were able to analyze the high level sample within 10% of the expected value. In the 0984 audit, 90% of the laboratories were able to analyze both sulfur samples within 10% of the expected value. Only 50% achieved 10% on the low moisture concentration in the 0984 audit; whereas, 75% in the 0384 audit achieved 10% on the low moisture concentration. For the ash analysis and Btu content, 92% to 100% of the reporting laboratories were able to achieve an accuracy within 10% for both sample concentrations.

The participants' accuracy improved with higher concentrations on all parameters except ash in the 0984 audit, where there was a slight decrease. For those laboratories that reported duplicate analyses, the intra-laboratory precision (repeatability) was not dependent on concentration level.

TABLE 14. SOURCE COAL AUDIT - 0384

Expected Value	No. of Analyses	Laboratories Accurate within ± 5%	Laboratories Accurate within ± 10%
		SULFUR	
0.45	(1)* 113	42%	60%
0.45	(2)* 100	37%	60%
3.28	(1) 113	23%	86%
3.28	(2) 99	28%	86%
		MOISTURE	
2.94	(1) 114	48%	75%
2.94	(2) 100	51%	78%
12.01	(1) 114	79%	92%
12.01	(2) 101	81%	93%
		ASH	
9.45	(1) 112	91%	94%
9.45	(2) 100	93%	94%
13.13	(1) 112	96%	98%
13.13	(2) 98	96%	99%
		GROSS CALORIFIC	
12115.	(1) 110	87%	89%
12115.	(2) 99	94%	95%
13135.	(1) 110	100%	100%
13135.	(2) 97	100%	100%

* Indicates first and second analyses

TABLE 15. SOURCE COAL AUDIT - 0984

Expected Value	No. of Analyses	Laboratories Accurate within ± 5%	Laboratories Accurate within ± 10%
		SULFUR	
1.17	(1)* 100	77%	95%
1.17	(2)* 95	77%	93%
2.93	(1) 99	64%	90%
2.93	(2) 95	63%	89%
		MOISTURE	
1.86	(1) 102	25%	48%
1.86	(2) 96	20%	51%
10.65	(1) 101	79%	92%
10.65	(2) 96	84%	93%
		ASH	
9.74	(1) 101	95%	97%
9.74	(2) 95	92%	97%
12.87	(1) 100	87%	92%
12.87	(2) 95	86%	92%
		GROSS CALORIFIC	
12595.	(1) 95	89%	96%
12595.	(2) 91	90%	96%
13710.	(1) 96	99%	99%
13710.	(2) 91	99%	99%

* Indicates first and second analyses

REFERENCES

1. U.S. Environmental Protection Agency. Standards of Performance for New Stationary Sources - Appendix A. Title 40, Part 60, Code of Federal Regulations.

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3. Streib, E. W. and M. R. Midgett. A Summary of the 1982 EPA National Performance Audit Program on Source Measurements. EPA-600/4-83-049, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, April 1984.

4. Streib, E. W., T. J. Logan and M. R. Midgett. A Summary of the 1983 EPA National Performance Audit Program on Source Measurements. EPA-600/4-85-004, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, January 1985.

5. Chauvenet, W. Manual of Spherical and Practical Astronomy: Volume II - Theory and Use of Astronomical Instruments (Method of Least Squares). J. P. Lippincott and Co., Philadelphia, Pennsylvania, 1863 (?).

6. American Society for Testing and Materials. Annual Book of ASTM Standards - 1984. Volume 5.05. 01-050584-13, American Society for Testing and Materials, Philadelphia, Pennsylvania.

APPENDIX A

FREQUENCY DISTRIBUTIONS

DGM FREQUENCY DISTRIBUTION OF ABSOLUTE PERCENT DIFFERENCE - 0684

# SAMP	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV	SKEWNESS	MEDIAN
631	.0	.3	.7	1.0	1.4	1.9	2.5	3.1	4.4	6.1	58.8	3.1	4.9	6.97	1.9
625	.0	.3	.7	1.0	1.4	1.8	2.4	3.1	4.2	5.9	17.1	2.8	2.9	-.12	1.9
611	.0	.3	.7	1.0	1.3	1.8	2.4	3.0	4.0	5.5	12.1	2.5	2.3	-.27	1.8
603	.0	.3	.6	1.0	1.3	1.7	2.3	2.9	3.8	5.2	9.6	2.4	2.1	-.38	1.7
599	.0	.3	.6	1.0	1.3	1.7	2.3	2.9	3.8	5.2	9.1	2.3	2.0	-.48	1.7
598	.0	.3	.6	1.0	1.3	1.7	2.3	2.9	3.7	5.2	8.9	2.3	2.0	-.56	1.7
596	.0	.3	.6	1.0	1.3	1.7	2.2	2.9	3.7	5.2	8.9	2.3	2.0	-.64	1.7
595	.0	.3	.6	1.0	1.3	1.7	2.2	2.8	3.7	5.1	8.7	2.3	1.9	-.71	1.7
593	.0	.3	.6	1.0	1.3	1.7	2.2	2.8	3.7	5.1	8.6	2.3	1.9	-.77	1.7
590	.0	.3	.6	1.0	1.3	1.7	2.2	2.8	3.6	5.1	8.5	2.2	1.9	-.83	1.7
587	.0	.3	.6	1.0	1.3	1.7	2.2	2.8	3.6	5.1	8.2	2.2	1.8	-.88	1.7
585	.0	.3	.6	.9	1.3	1.7	2.2	2.8	3.5	5.0	8.0	2.2	1.8	-.93	1.7

SO_2 FREQUENCY DISTRIBUTION OF PERCENT DIFFERENCE - NO OUTLIERS REMOVED

AUDIT 0584

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
2	91	.00	.27	.74	1.14	1.51	2.15	2.56	3.56	6.52	10.26	300.13	7.10	31.42
3	92	.00	.43	.67	1.13	1.45	1.88	2.69	3.40	4.32	9.14	275.62	7.10	29.24
5	92	.00	.36	.54	.87	1.09	1.60	1.87	2.55	3.25	5.16	296.49	5.69	30.81
7	92	.00	.26	.61	1.09	1.44	1.77	2.22	2.63	3.49	5.01	293.38	5.57	30.42
9	92	.00	.20	.45	.61	.90	1.36	1.65	1.99	3.12	4.15	300.90	5.21	31.24

NO_x FREQUENCY DISTRIBUTION OF PERCENT DIFFERENCE - NO OUTLIERS REMOVED

AUDIT 0484

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
1	70	.11	.67	1.44	1.83	2.43	4.36	6.12	9.11	11.46	18.74	127.74	10.41	20.33
4	70	.00	.63	.90	1.78	2.35	3.50	4.36	5.33	10.09	16.17	87.46	9.18	17.67
6	71	.00	.99	2.75	4.40	5.27	6.92	7.69	10.99	15.27	31.87	278.02	16.83	36.30
8	71	.11	.73	1.37	2.79	3.52	4.40	5.66	7.20	10.38	16.66	117.13	11.44	22.48
9	70	.29	1.17	2.25	2.83	3.81	5.08	7.03	10.64	15.82	38.67	347.46	18.09	45.59

NATIONAL COAL AUDIT FREQUENCY DISTRIBUTION

OF ABSOLUTE PERCENT DIFFERENCES OF EXPECTED AND REPORTED VALUES - STUDY 0384

SULFUR

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
4000	212	.00	3.35	4.57	5.18	6.10	6.71	7.32	8.23	9.15	10.37	88.11	7.80	8.47
7000	213	.00	2.22	2.22	4.44	6.67	8.89	8.89	13.33	15.56	24.44	535.56	16.03	51.99

MOISTURE

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
4000	214	.00	1.36	2.38	3.40	4.42	5.44	6.46	8.16	10.88	14.97	104.76	7.83	9.97
7000	215	.00	.58	1.00	1.33	1.75	2.25	2.83	3.50	5.00	7.16	97.59	4.38	10.30

ASH

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
4000	210	.00	.15	.23	.38	.53	.61	.76	.99	1.37	2.36	76.69	1.54	5.58
7000	212	.00	.21	.42	.74	.95	1.16	1.59	1.80	2.43	3.28	32.80	2.40	4.39

GROSS CAL

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
4000	207	.01	.05	.11	.20	.27	.40	.55	.73	.97	1.36	4.59	.65	.75
7000	209	.00	.06	.17	.26	.34	.40	.54	.67	.93	2.48	13.02	1.31	2.84

NATIONAL COAL AUDIT FREQUENCY DISTRIBUTION

OF ABSOLUTE PERCENT DIFFERENCES OF EXPECTED AND REPORTED VALUES - STUDY 0984

SULFUR

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
5000	195	.00	.85	.85	1.71	1.71	2.56	3.42	4.27	5.13	8.55	101.71	4.36	9.62
8000	194	.00	.34	1.02	1.71	2.73	3.75	4.78	5.80	7.17	9.90	44.71	5.06	5.79

MOISTURE

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
5000	198	.00	2.15	4.30	6.99	8.06	10.22	11.29	13.44	16.13	22.04	89.25	12.78	12.84
8000	197	.00	.66	1.22	1.88	2.25	2.72	3.38	3.94	4.79	6.20	90.61	5.35	12.94

ASH

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
5000	196	.00	.21	.31	.51	.72	.92	1.13	1.64	2.05	3.90	250.10	4.12	24.51
8000	195	.00	.08	.23	.47	.62	.85	1.01	1.40	2.18	7.23	113.68	3.18	10.22

GROSS CAL

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
5000	187	.06	.50	.74	.85	.97	1.09	1.20	1.26	1.39	1.54	15.28	1.22	1.53
8000	186	.02	.21	.37	.52	.67	.78	.91	1.05	1.71	4.92	12.18	1.84	2.82

NATIONAL COAL AUDIT FREQUENCY DISTRIBUTION

OF ABSOLUTE PERCENT DIFFERENCES OF EXPECTED AND REPORTED VALUES - STUDY 0784

CO_2

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
4000	126	.00	.00	1.25	2.50	2.50	2.50	3.75	5.00	5.00	7.50	45.00	4.41	6.53

O_2

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
4000	126	.00	1.01	1.01	1.01	1.01	2.02	3.03	3.03	4.04	5.05	75.76	4.74	11.38

CO

Sample No.	NO.	MIN	10%	20%	30%	40%	50%	60%	70%	80%	90%	MAX	MEAN	STDEV
4000	101	.00	.00	14.29	14.29	14.29	14.29	28.57	28.57	42.86	57.14	85.71	26.17	21.19

APPENDIX B

INSTRUCTIONS FOR EPA AUDIT MATERIALS

INSTRUCTIONS FOR USING EPA METHOD 3 AUDIT MATERIALS

Equipment Supplied with Audit Kit

(1) Small gas cylinder containing four liters of gas

(2) Nozzle for cylinder (taped on cylinder)

(3) Tygon tubing

Equipment to be Supplied by Participant

(1) Orsat analyzer

(2) Clamp

(3) Extra Tygon or surgical tubing

Procedure

(1) Leak-check apparatus by clamping off tubing. SEE DIAGRAM.

(2) Fill up burette with gas by using positive pressure. Vent this sample through the manifold to the atmosphere.

(3) Repeat Step 2.

(4) Fill up burette past fill mark with the gas and carefully vent out excess to the atmosphere, until the fill mark is reached.

(5) Analyze for CO_2, O_2 and CO as described in Sections 4.2.5, 4.2.6 and 4.2.7 of EPA Method 3.

(6) Record the results on the data card enclosed with the sample.

(7) Repeat Steps 4 through 6.

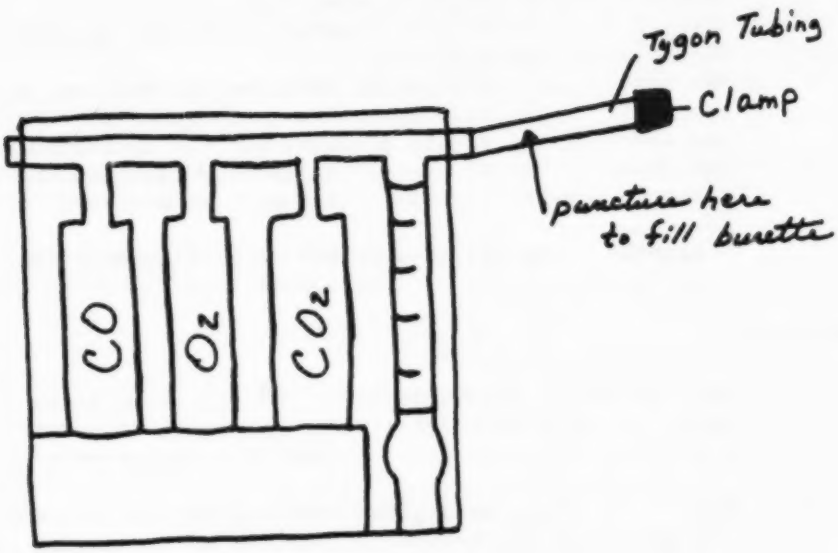
CAUTION: If the tubing is punctured excess times, leakage can occur. Replace if necessary.

Send the data card to the address below. (The cylinder gas can should not be returned.)

Ms. Ellen Streib
Quality Assurance Division (MD-77A)
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Note: Site number will always be 001 except when other Orsat apparatus or participants are using the same gas sample. The extra apparatus or participants should be labeled 002, 003, etc.

APPARATUS SET-UP



INSTRUCTIONS FOR USE OF ENVIRONMENTAL PROTECTION AGENCY
METHOD 5 DRY GAS METER PERFORMANCE TEST DEVICE

NOTE: All procedures referred to are from revised Method 5 published in the Federal Register, Volume 12, Number 160, Part II. Thursday, August 18, 1977, pp. 41776-41782 and references contained therein. This revised method should be adhered to in all details in the use of this quality assurance performance device.

EQUIPMENT: The participant in this study should possess the following equipment, including the performance test device supplied by EPA.

Quantity	Item
1	Method 5/Source Sampling Meter Box
1	Stopwatch, preferably calibrated in decimal minutes
1	Thermometer, ambient range
1	Barometer. If unavailable, call nearest National Weather Service and request the ABSOLUTE barometric pressure. (Corrected for temperature and acceleration due to gravity, but not corrected for altitude.)
1	Performance Test Device. A calibrated flow orifice housed in a quick-connect coupling and identified with an engraved three-digit serial number. WARNING: THE DEVICE MUST NOT BE DISASSEMBLED UNDER ANY CIRCUMSTANCES. Use these devices at room temperature.

PROCEDURE:

1. Calibration of Vacuum Gauge -- The vacuum pressure gauge on the meter box must be calibrated in the range of use (11-22" Hg) against a standard (Hg Manometer) to ensure accurate results.

2. Remove the performance test device from its case and insert it into the gas inlet quick-connect coupling on the source sampling meter box.

3. Turn the power to the meter box on and start the pump.

4. Adjust the coarse flow rate control valve and the fine flow rate control valve to give a reading of 19" Hg (vacuum reading).
   CAUTION: The vacuum reading must be accurate and stable for the test period.

5. Allow the orifice and source sampling meter box to warm up for 45 minutes with flow controls adjusted as described in Step 3 before starting quality assurance runs.

PROCEDURE: (continued)

6 Make triplicate quality assurance runs. For each run, record initial and final dry gas meter volumes, dry gas meter inlet and outlet temperatures, internal orifice pressure drop (ΔH), ambient temperature, and barometric pressure. Run duration should be slightly greater than 15 minutes. The following procedure is recommended. Fifteen minutes after a run is started, the participant watches the dry gas meter needle closely. As the needle reaches the zero (12 o'clock) position, the pump and stopwatch are stopped simultaneously. The dry gas meter volume and time are recorded.

This complete run procedure is performed three times to provide the required triplicate quality assurance runs.

7 Calculate the corrected dry gas volume for each run using equation 5.1 of the above-referenced Method 5. For each replicate, record the corrected dry gas volume in dry standard cubic meters, the sampling time in decimal minutes, the barometric pressure in mm Hg, and the ambient temperature in degrees Celcius on the enclosed data card. Be sure to record the performance test device serial number on the data card in the column headed "Orifice Number."

NOTE 1: If you calculate dry gas volume in English Units, use the conversion factor of 0.02832 m^3ft^3 to obtain the volume in metric units.

NOTE 2: If your stopwatch is not in decimal minutes, be sure to convert (e.g. 15 minutes 20 seconds is reported as 15.33 minutes).

8 After recording the requested data on the enclosed data form, return the data form and the performance test device to:

Quality Assurance Division (MD-77A)
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711
ATTN: Ellen W. Streib

A postpaid return envelope and label are enclosed for this purpose.

INSTRUCTIONS FOR USE OF ENVIRONMENTAL PROTECTION AGENCY STATIONARY SOURCE QUALITY ASSURANCE SO_2 REFERENCE SAMPLES

NOTE: All Method 6 procedures referred to are from the amended method published in the Federal Register Vol. 42, No. 160, Part II, Thursday, August 18, 1977, pp 41782-41784. This amended method should be adhered to in all details in the analysis of these reference standards.

1. Prepare 3 percent hydrogen peroxide according to Section 3.1.3 of the method (30 ml is required for each sample and each blank).

2. Prepare each reference sample for analysis as follows: Wrap a paper towel around the ampoule and with the ampoule in an upright position break off the top at the prescored mark by exerting pressure sideways. From the ampoule pipette exactly 5 ml of the reference sample into a 100 ml volumetric flask. Add 30 ml of 3 percent hydrogen peroxide solution. Dilute exactly to the mark with deionized, distilled water. Analyze the sample in accordance with the procedure detailed in Section 4.3 of the method, beginning with "Pipette a 20 ml aliquot of this solution..." (Note: If more than 50 ml of barium perchlorate titrant is required for any sample analysis, a smaller aliquot should be selected to allow titration with less than 50 ml titrant.)

3. Calculate the concentration, C_{SO2} (concentration of sulfur dioxide, dry basis, corrected to standard conditions, mg/dscm), using Equation 6-2. A value of 21×10^{-3} dscm should be used for $V_m(std)$, in the equation. A value of 100 ml should be used for V_{soln} in the equation.

4. Record the reference standard sample numbers and their corresponding SO_2 concentrations in mg/dscm on the enclosed data form. Return the form to:

Quality Assurance Division (MD-77A)
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711
ATTN: Ellen W. Streib

If other than EPA Method 6 is used for your analyses, please explain in detail your analytical procedure on the back of the enclosed data form.

INSTRUCTIONS FOR USE OF ENVIRONMENTAL PROTECTION AGENCY STATIONARY SOURCE QUALITY ASSURANCE NO_x REFERENCE SAMPLES

Note: All Method 7 procedures referred to are from the amended method published in the Federal Register Vol. 42, No. 160, Part 11, Thursday, August 18, 1977, pp 41784-41786. This amended method should be adhered to in all details in the analysis of these reference standards.

1. Prepare absorbing solution according to Section 3.1 of the method.

2. Prepare each reference sample for analysis as follows: Wrap a paper towel around the ampule and with the ampule in an upright position break off the top at the prescored mark by exerting pressure sideways. From the ampule pipette exactly 5 ml of the reference sample into a 100-ml beaker. Add 25 ml absorbing solution to the beaker; adjust the pH to 9-12 (using pH paper as indicated in Section 4.2 of the method) by dropwise addition of sodium hydroxide (1N). Quantitatively transfer the contents of the beaker to a 50-ml volumetric flask and dilute exactly to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot of the diluted sample into a porcelain evaporating dish. Beginning with the evaporation step in Section 4.3, complete the sample analysis.

3. Calculate total µg NO_2 per sample using Equation 7-3. Calculate the sample concentration, C (concentration of NO_x as NO_2, dry basis, corrected to standard conditions, mg/dscm), using Equation 7-4. A value of 2000 ml should be used for V_{sc} in Equation 7-4.

4. Record the reference sample numbers and their corresponding concentrations, C, in mg/dscm on the enclosed data form. Return the form to:

Quality Assurance Division (MD-77A)
Environmental Monitoring Systems Laboratory
Environmental Protection Agency
Research Triangle Park, NC 27711
ATTN: Ellen W. Streib

If other than EPA Method 7 is used for your analyses, please explain in detail your analytical procedure on the back of the enclosed data form.

COAL AUDIT PROGRAM INFORMATION

1. There is approximately 50 grams of 60 mesh coal per bottle.

2. Analyze the coal samples for moisture and on a dry basis for ash, sulfur and gross calorific value. Report moisture, ash, and sulfur in weight percent with gross calorific value reported as BTU/lb.

3. All methods used in the analysis of these coal samples should follow American Society for Testing and Materials (ASTM) recommended procedures or an accepted automatic analytical device.

4. Suggested procedures are:

Moisture	D-3173
Ash	D-3174
Sulfur	D-3177
Gross Calorific Value	D-2015

   Please note on the data card (columns 17-32) the ASTM method number. If an ASTM method was not used for analysis note that on the back of the data card. Be parameter specific.

5. If you cannot analyze the coal sample for all four parameters, analyze for what you can. Analysis of moisture is necessary to calculate on a dry basis any of the other three parameters. Analysis of sulfur is also necessary for the calculation of gross calorific value.

6. Analyze each sample in duplicate (if possible) and record results as analysis 1 and analysis 2 for each parameter.

7. Most laboratories will use site number 001. Multiple site numbers are used by laboratories that receive more than one set of samples. These central laboratories have requested auditing of their satellite laboratories.

8. After recording the requested data on the enclosed data card, return the data card to:

   Ms. Ellen W. Streib
   Quality Assurance Division (MD-77)
   Environmental Monitoring Systems Laboratory
   U.S. Environmental Protection Agency
   Research Triangle Park, NC 27711

   A postpaid return envelope is enclosed for this purpose.

9. If you have any questions concerning this or any source method audit, please call (919/541-7834).

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